ON THE SYNTHESIS OF CERTAIN HALOGEN-CONTAINING AZO DYES, AND THE EFFECT OF THE HALOGEN ON THE COLOR

By

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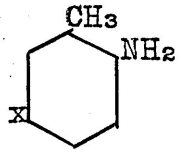
TABLE OF CONTENTS.

Part I. Preparation of Bases and Dyes.

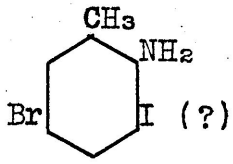
Part II. Application of the Dyes on Cotton, Wool and Silk with and without a Mordant.

ON THE SYNTHESIS OF CERTAIN HALOGEN-CONTAINING AZO DYES, AND THE EFFECT OF THE HALOGEN ON THE COLOR

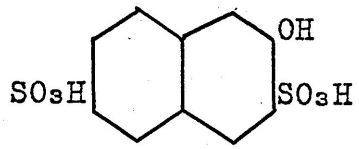
The object of this work was to show what effects the different halogens have on the color. The base used was o-toluidine, except in Preparation XIII; all the halogens were introduced in the p-position with respect to the NH_2 group.



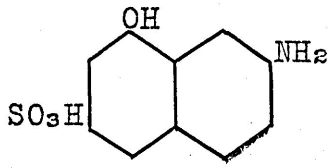
x = Cl, Br or I.



The acid coupled with was R and G (Amidonaphthol sulphonic acid G, or gamma acid).



R acid



G acid

The first part of the work was taken up in preparing the different halogen derivatives and coupling them with R and G acid.

PREPARATION I.

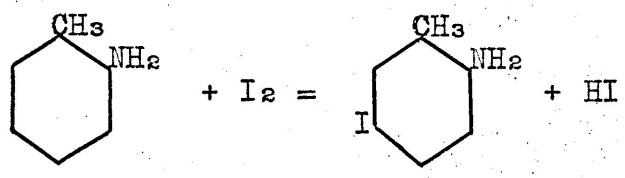
The first compound made was 1-CH_3-2-NH_2-5-I-C_6H_3.

Material:

26 grams o-toluidine (redistilled B.P. 195°).
61.2 grams iodine.
25 grams calcium carbonate.
60 c.c. ether.
60 c.c. water.

The mixture was heated on a water-bath, using a reflux. The reaction was complete after all the iodine had gone into solution, and iodine vapors ceased to be given off (4 hours).

The resulting product was steam distilled. A white to purple oil distilled, which on standing solidified. On recrystallizing from gasoline the crystals were grayish white. M. P. 87°. The M.P. given by the authors, 91-92°.



$$HI + CaCO_3 = CaI + H_2O + CO_2$$

PREPARATION II.

Coupling 1-CH_3-2-NH_2-5-I-C_6H_3 through the diazo reaction with the sodium salt of R acid.

Material:

7 grams 1-CH_3-2-NH_2-5-I-C_6H_3.
2.1 grams sodium nitrite.
10 c.c. hydrochloric acid.
9.2 grams R acid.

Procedure:

The base was dissolved in dilute hydrochloric acid, with the application of a little heat. This was now cooled to +2° C. and diazotized with sodium nitrite, using the starch iodine test.

The R acid was dissolved in sodium hydroxide, cooled to +2° C. and the diazo compound added to it slowly. Care was taken that the temperature did not rise above 5° C.

The solution is now a deep-red color. On adding a saturated salt solution the dye precipitated out. This was filtered off and dried at 110° C.

Analysis:

	I	II	III	IV	V	VI	VII
Weight of dye	.1762	.1570	.3657	.1501	.1256	.2122	.1440
Weight of Na_2SO_4	.1098	.0641	.0664	.0239	.0185	.0369	.0245
Percent Na	20.67	13.20	5.88	5.14	4.77	5.63	5.51
Percent Na theo.	7.77						

Analysis I was run before the sample was washed.

II " " after one washing.

III " " " washing that left from II.

IV " " " " " " " III.

V " " " " " " " IV twice.

VI and VII were run after washing the original, using three different waters.

Method of Washing:

The dye was placed in a test tube and shaken vigorously with cold water. The water was filtered off immediately on account of the solubility of the dye. It was then dried at 110°. A small sample was then weighed out into a crucible, heated gently. A few drops of c. p. H_2SO_4 were added. On heating the iodine volatilized first, then the compound charred down. On retreating it with H_2SO_4 and driving off the excess a perfectly white precipitate of Na_2SO_4 was obtained. It is yellow, hot, but white when cold.

PREPARATION III.

Coupling 1-CH_3-2-NH_2-5-I-C_6H_3 through the diazo reaction with the sodium salt of G acid.

Material:

7 grams 1-CH_3-2-NH_2-5-I-C_6H_3.
2.1 grams sodium nitrite.
10 c.c. hydrochloric acid.
7.2 grams G acid.

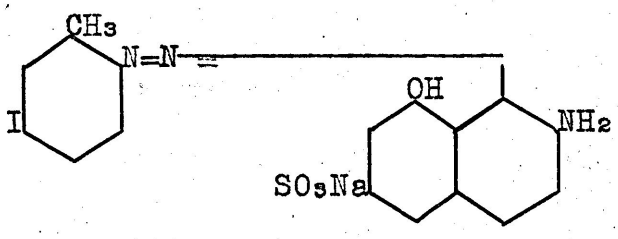
The base was dissolved in dilute HCl. Cooled to +2° and diazotized with $NaNO_2$. The G acid was dissolved in NaOH. Cooled to +2°. The solution was mechanically stirred. The diazo compound was added to it. After stirring for thirty minutes a saturated salt solution was added. The dye precipitated out. It was filtered and dried.

Analysis:

	I	II	III	IV
Weight od dye	.1764	.1853	.4775	.1056
Weight of Na_2SO_4	.0680	.0739	.0688	.0154
Percent Na	12.48	12.90	4.66	4.72
Percent Na theo.	4.55			

Analysis I and II were run before washing the dye.

III and IV, after washing the dye with water.



PREPARATION IV.

Preparing p-Br-o-toluidine directly.

Material:

26 grams 1-CH_3-2-NH_2-C_6H_6.
36 grams bromine.
25 grams calcium carbonate.
60 c.c. ether.
60 c.c. water.

All these reagents were mixed together, except the bromine. The solution was now cooled, and the bromine added carefully with constant stirring. It was then heated on a reflux four hours. The ether was then distilled off. The liquid was steam distilled. Recovery of one gram of product which melted at 54°. The M.P. of para-Br-o-toluidine is 58°. This method was abandoned.

PREPARATION V.

Preparing p-Br-o-toluidine thru the acetyl derivative.

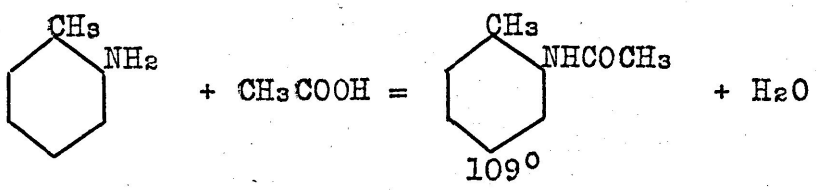
Material:

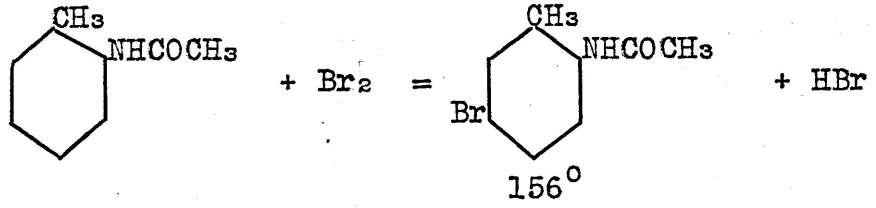
107 grams o-toluidine.
60 glacial acetic acid.

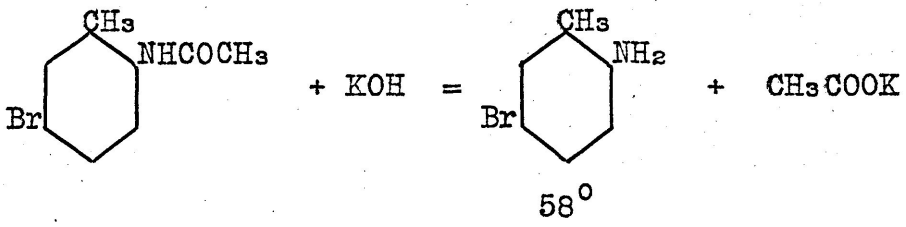
This mixture was boiled, using a reflux condenser, for fifteen hours. Precipitated by pouring into cold water. M.P. 109°.

40.5 grams of the acetyl derivative was dissolved in 150 grams of glacial acetic acid. Cooled in the ice bath. The solution was stirred automatically. 48 grams of bromine was added. The mixture was then allowed to come to room temperature and poured into water. It was filtered and dried. The yield was 95% of the theoretical.

This p-Br-acet-o-toluidine was treated with 48 grams of KOH in 400 c.c. of alcohol under a reflux condenser for 24 hours. The alcohol was then distilled off. Water was added, and the solution steam distilled to drive over the p-Br-o-toluidine. It was recrystallized from gasoline. M.P. 58°. Yield 37 grams. (64%).







PREPARATION VI.

Coupling p-Br-o-toluidine thru the diazo reaction with the sodium salt of R acid.

Material:

5.5 grams p-Br-o-toluidine.
2 grams sodium nitrite.
10 c.c. hydrochloric acid.
8.9 grams R acid.

The p-Br-o-toluidine was dissolved in dilute HCl. The solution was next cooled to +2°. It was automatically stirred while a cold solution of sodium nitrite was added. The excess sodium nitrite was noted by the starch-iodine test.

The R acid was dissolved in NaOH and cooled to +2°. Next the diazo compound was added, care being taken not to let the temperature rise above +5°. An excess of NaOH

was added so that the solution was always alkaline. Solution deep red color. Adding a saturated salt solution, the dye precipitated out.

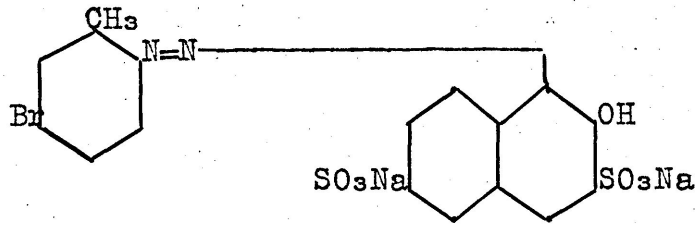
Analysis:

	I	II	III
Weight of dye	.1022	.3463	.3943
Weight of Na_2SO_4	.0510	.1000	.1034
Percent Na	16.50	9.34	8.48
Percent Na theo.	8.44		

Analysis I was run without washing the dye.

II was washed and dried once.

III was made by rewashing and drying that left from II.



PREPARATION VII

Coupling p-Br-o-toluidine with G acid (sodium salt) thru the diazo reaction.

Material:

7 grams p-Br-o-toluidine.
2.6 grams sodium nitrite.
10 c.c. hydrochloric acid.
9.1 grams G acid.

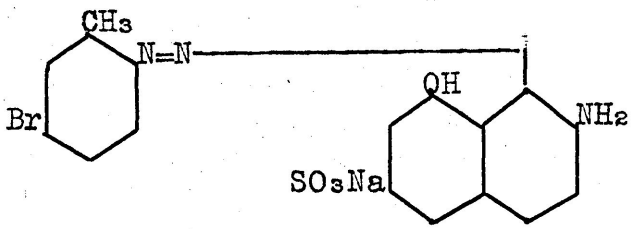
The base was dissolved in dilute HCl. Cooled to $+2^{o}$, and diazotized with sodium nitrite. Mechanically stirred. The G acid was dissolved in NaOH. An excess of NaOH was added to neutralize the excess acid from the diazo compound. It was then cooled to $+2^{o}$ and the diazo compound added to it. After stirring fifteen minutes the dye was precipitated out, using a saturated solution.

Analysis:

	I	II
Weight of dye	.1032	.2639
Weight of Na_2SO_4	.0272	.0385
Percent Na	8.50	4.72
Percent Na theo.	5.02	

Analysis I was run without washing.

II was run after washing I once.



PREPARATION VIII.

Preparing p-Cl-o-toluidine.

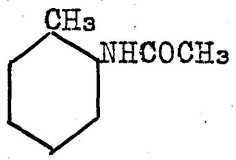
Material:

53 grams acet-o-toluidine.
100 grams acetic acid (glacial).

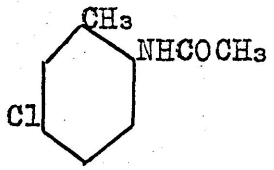
52 grams bleaching powder.
50 grams KOH.
125 c.c. alcohol.

The acet-o-toluidine was dissolved, by gently warming, in a mixture of glacial acetic acid and alcohol. The solution was next diluted to 1000 c.c. and heated to 50°. At this temperature a cold solution of bleaching powder was added. During the addition of the bleaching powder the mixture was continually stirred. The p-Cl-acet-o-toluidine was collected, washed with water, and re-crystallized from alcohol.

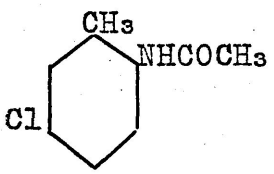
The p-Cl-acet-o-toluidine was dissolved in 125 c.c. of alcohol and hydrolyzed with 50 grams of KOH, boiling for twelve hours on a reflux. The alcohol was distilled off, then the p-Cl-o-toluidine was steam distilled. M.P. 29°.



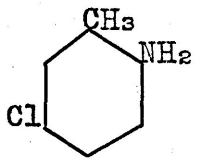
$$+ CaOCl_2 + 2CH_3COOH =$$



$$+ (CH_3COO)_2Ca + HCl + H_2O$$



$$+ KOH =$$



$$+ CH_3COOK.$$

PREPARATION IX

Coupling p-Cl-o-toluidine with the sodium salt of R acid thru the diazo reaction.

Material:

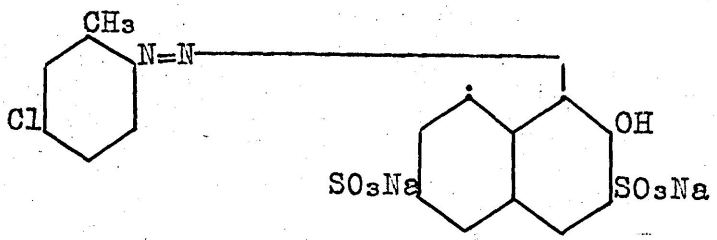
4.5 grams p-Cl-o-toluidine.
2.2 grams sodium nitrite.
10 c.c. hydrochloric acid.
9.7 grams R acid.

The base was dissolved in dilute HCl. Cooled to $+2^{\circ}$ and diazotized with sodium nitrite. The R acid was dissolved in NaOH. After cooling it to $+2^{\circ}$ the cold diazo solution was added to it. A small excess of NaOH was added to neutralize any excess acid from the diazo compound. After stirring for thirty minutes and adding a saturated salt solution the dye precipitated out.

Analysis:

	I	II	III
Weight of dye	.1794	.1818	.1710
Weight of Na_2SO_4	.0645	.0611	.0503
Percent Na	11.86	10.87	9.50
Percent Na theo.	9.19		

Analysis III was run after rewashing that left from Analysis II.



PREPARATION X.

Coupling p-Cl-o-toluidine with G acid (sodium salt) thru the diazo reaction.

Material:

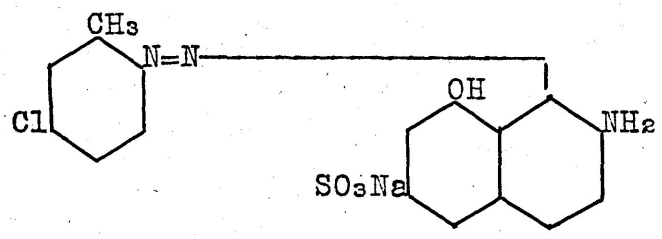
4.5 grams p-Cl-o-toluidine.
2.2 grams sodium nitrite.
10 c.c. hydrochloric acid.
7.6 grams G acid.

The base was dissolved in dilute acid. Cooled to +2° and diazotized with sodium nitrite. The G acid was next dissolved in NaOH. Cooled to +2° and the diazo compound added to it. After stirring thirty minutes the dye was precipitated out with saturated salt solution.

Analysis:

	I	II
Weight of dye	.1260	.1528
Weight of Na_2SO_4	.0214	.0251
Percent Na	5.48	5.31
Percent Na theo.	5.56	

Analyses I and II were run after rewashing the dye once with water.

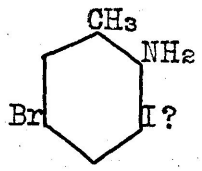


PREPARATION XI.

Preparing 1-CH_3-2-NH_2-3?-I-5-Br-C_6H_6.

Material:

10 grams p-Br-o-toluidine.
14 grams iodine.
12 grams calcium carbonate.
30 c.c. ether.
30 c.c. water.



This mixture was heated on a water bath for fifteen hours, using a reflux. The ether was distilled off, then the resulting product was steam distilled. A white flocculent precipitate, insoluble in water, came over. This was recrystallized from gasoline. M.P. 62°.

Analysis:

For nitrogen by the Kjeldahl method.

	I	II
Weight of sample	.2660	.4668
	25 c.c. N/15 HCl used. 16.1 c.c. NaOH used to neutralize the excess. 16.1x1.19 = 19.15. 25.00 19.15 5.85	25.2 c.c. N/15 HCl used. 12.7 c.c. NaOH used to neutralize the excess. 12.7 x 1.19 = 15.11. 25.20 15.11 10.09
	1 c.c. HCl = .0021 grams N.	
	$\frac{.0021 \times 5.85}{.2660} = 4.63\%$ N.	$\frac{.0021 \times 10.09}{.4668} = 4.54\%$ N.

The ratio of HCl to NaOH is 1.19 : 1.

Percentage of nitrogen (theoretical), 4.66.

PREPARATION XII.

The hydrochloride salt of 1-CH_3-2-NH_2-3?-I-5-Br-C_6H_3.

The 1-CH_3-2-NH_2-3?-I-5-Br-C_6H_3 was dissolved in c.p. C_6H_6, then dry HCl gas was passed in until the precipitation was complete. The C_6H_6 was evaporated off on a water bath, finally drying in a desiccator over H_2SO_4.

Analysis:

	I	II
Weight of sample	.1560	.2530
The sample was dissolved in warm water.		
23.6 c.c. N/150 NaOH used to neutralize the acid liberated.		39.40 c.c. N/150 NaOH used to neutralize the acid liberated.
2.36 x 1.19 = 2.808 c.c. HCl.		3.94 x 1.19 = 4.688 c.c. HCl.
N/15 HCl = .0005469 grams HCl per c.c.		
$\frac{2.808 \times .0005469}{.1560}$ = 9.48% HCl		$\frac{4.688 \times .0005469}{.2530}$ = 10.14% HCl.

The ratio of HCl to NaOH is 1.19 : 1.

Percentage of HCl (theoretical), 10.23.

PREPARATION XIII.

Preparing the acetyl derivative of 1-CH_3-2-NH_2-3?-I-5-Br-C_6H_3.

The 1-CH_3-2-NH_2-3?-I-5-Br-C_6H_3 was treated with acetic anhydride. The product formed was filtered off and dried. M.P. 154°.

On account of lack of time was unable to make further analysis.

PREPARATION XIV.

Coupling 1-CH_3-2-NH_2-3?-I-5-Br-C_6H_6 with R acid thru the diazo reaction.

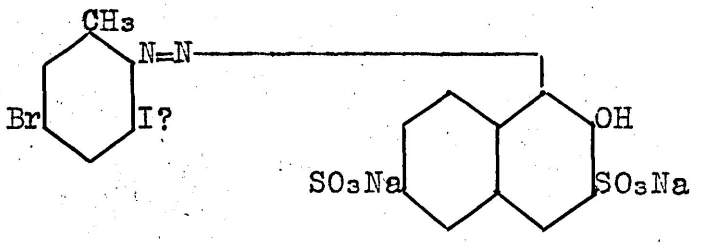
Material:

2.5 grams 1-CH_3-2-NH_2-3?-I-5-Br-C_6H_6.
.7 gram sodium nitrite.
10 c.c. hydrochloric acid.
2.5 grams R acid.

The base was dissolved in dilute HCl. The solution was automatically stirred. After cooling in an ice bath to $+2^{\circ}$ it was diazotized with $NaNO_2$.

The R acid was dissolved in NaOH, cooled to $+2^{\circ}$. The diazo compound was added to it carefully, so that the temperature did not rise above $+5^{\circ}$.

On account of the small quantity of dye an analysis was not run on the final dye-stuff. A saturated salt solution was added as in the other dyes, but the dye did not precipitate out even after stirring for sixty minutes. This solution was used in dyeing the material.



PREPARATION XV.

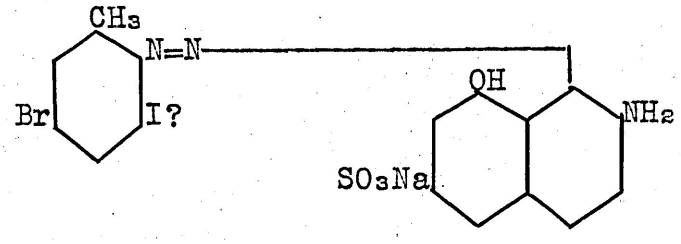
Coupling 1-CH_3-2-NH_2-3?-I-5-Br-C_6H_6 with G acid (sodium salt) thru the diazo reaction.

Material:

2.5 grams 1-CH_3-2-NH_2-3?-I-5-Br-C_6H_6.
.7 gram sodium nitrite.
10 c.c. hydrochloric acid.
1.95 grams G acid.

The base was dissolved in dilute HCl, cooled to $+2^{\circ}$, and diazotized with Na NO_2. The sodium salt of G acid was made by dissolving it in NaOH. The diazo compound was next added to it. After stirring for thirty minutes a saturated salt solution was added.

On account of lack of time no analyses were run on the product.



PART II.

APPLICATION OF THE DIFFERENT DYES TO COTTON, WOOL AND SILK, WITH AND WITHOUT A MORDANT

General Theory of Dyeing.

The chemical theory supposes that dyeing involves a chemical reaction between the fibre and the dye-stuff, and that a definite chemical compound known as a color lake is produced.

The mechanical theory considers the effect of dyeing to be simply a deposit of colored particles in the substance of the fibre and the combination so formed to be merely a mechanical mixture.

The chemical theory is supported by the fact that wool and silk exhibit well defined chemical reactions of acid and basic character.

Acid dyes are principally used for the dyeing of wool and silk, and only to a limited extent for the dyeing of cotton. The baths are either made acid with H_2SO_4 or CH_3COOH.

Basic dyes are used chiefly for dyeing cotton and silk. They are applied to the animal fibres directly from neutral baths. For cotton a mordant of acid

character is used (tannin).

The mordant dyes are exclusively used for the dyeing of wool. These dyes do not have a direct affinity for any of the fibres, and require the use of a metallic mordant in their application.

Substantive dyes are so called because they have a direct affinity for all fibres. They are principally cotton dyes.

Application of Dye Stuffs.

General method of dyeing without a mordant:

Bath 300 c.c. water.
60% Na_2SO_4.)
10% H_2SO_4. (1 : 10).) Based on the weight of the cloth used.
7% dye.)
Temperature of bath 140° F. to start.
Place material in bath, turn every few minutes, so that the material is dyed evenly.
Let simmer one-half hour.
Remove and wash with water until wash water is clear.

The Na_2SO_4 acts as a retarding agent, causing the dye to color more evenly. The general ratio of material to bath is 1 gram of material per 100 grams of water.

In figuring the bath, it is made up according to the amount of material to be dyed.

Example:

For 3.6 grams of cloth.

3.6 x .07 = .242 grams of dye.
3.6 x .10 = .36 grams H_2SO_4.
3.6 x .6 = 2.40 grams Na_2SO_4.

Precautions:

(1) Start the dye bath at a low temperature and heat gradually to the boiling point.

(2) Do not add any acid until the dye has been thoroughly worked into the material, and then add the acid in several portions during the dyeing.

(3) Be sure that the dye stuff is dissolved.

(4) Do not use a short bath, i.e., one not less than 300 c.c.

(5) Cloth must not be put in the bath dry.

Mordant Baths.

Chrome Mordant:

Bath 300 c.c. water.
1.5 grams $K_2Cr_2O_7$ + 1.5 grams $KHC_4H_4O_6$ was added; bath was allowed to simmer thirty minutes.
Total grams of cloth added, 22.
Samples of cotton, wool and silk were used.

Iron Mordant:

The bath was same as above, except that 4 grams of $FeSO_4$ were used instead of $K_2Cr_2O_7$.

Alum Mordant:

The bath was same as above, except that 1.5 grams of $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$ were used instead of $K_2Cr_2O_7$.

Tin Mordant:

The bath was the same as above, except that 0.5 gram of stannous chloride was used instead of the $K_2Cr_2O_7$ and that 1.0 gram of oxalic acid was used instead of the tartrate.

Tannin Mordant:

The bath was the same as above, except that 0.5 gram of tannic acid was used instead of the $K_2Cr_2O_7$ and that 5.0 grams of tartar-emetic was used instead of the tartrate.

Typical Methods of Dyeing.

The $(IR)^+$ colors will be explained; this applies to all the others as well.

The bath was made up as stated. The same amount of dye was used in all the baths. Strips of cotton, wool and silk unmordanted were placed in the same bath. Strips of cotton, wool and silk mordanted with $K_2Cr_2O_7$ were placed in a different bath. Each bath received the same treatment.

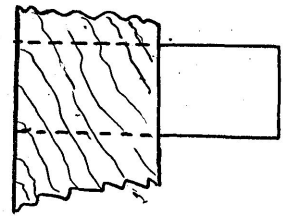
By using the same concentration of all the baths it was possible to contrast the color and see what effect the iodine, bromine, or chlorine had on the color.

+Meaning the dye formed by coupling 1-CH_3-2-NH_2-5-I-C_6H_3 with the sodium salt of R acid. (BrR) would have the same significance.

After the material had been dyed each set of dyed material was placed in a labelled envelope.

Exposure Treatment.

All the samples except the (IBrR) and the (IBrG) colors were exposed to the weather for four weeks. This was done to see what effect light and air had on the colors. Each sample was tacked on a board, one-half exposed to the air while the other half was covered.



No change could be noticed on the wool and silk, but the effect on the cotton can be seen by referring to the (IR) samples.

By looking at the silk carefully one can see that the mordant in some cases gives a brighter and in other cases a duller color. For example, in the (IR) samples the iron is darker than the tannin.

The Effect of the Halogen on the Color.

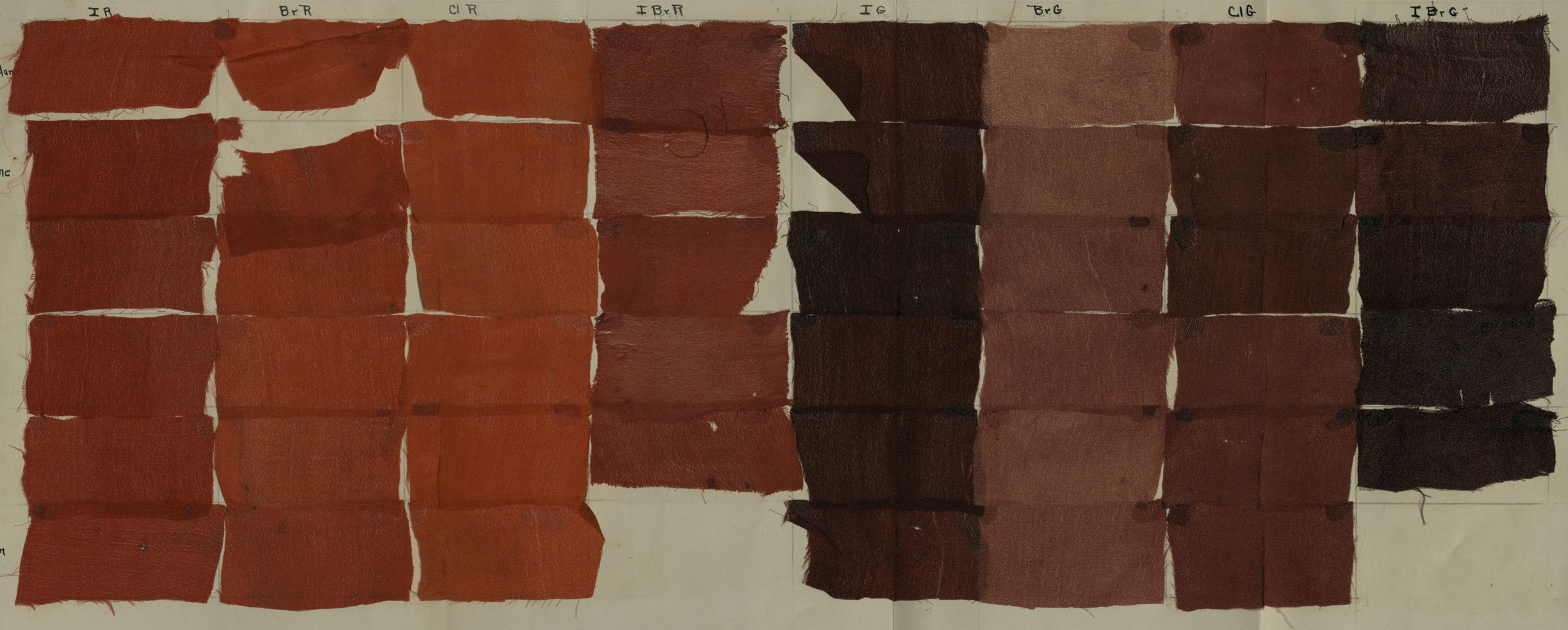
The iodine compounds with the higher molar weight give a darker color. The bromine compounds give a lighter shade. The chlorine compounds give a still lighter color. For example, the (IR), (BrR), (ClR) on silk. The iodine-brom compounds give a darker color than either the iodine or bromine compounds.

This is logical. The higher the molar weight, the darker the color.

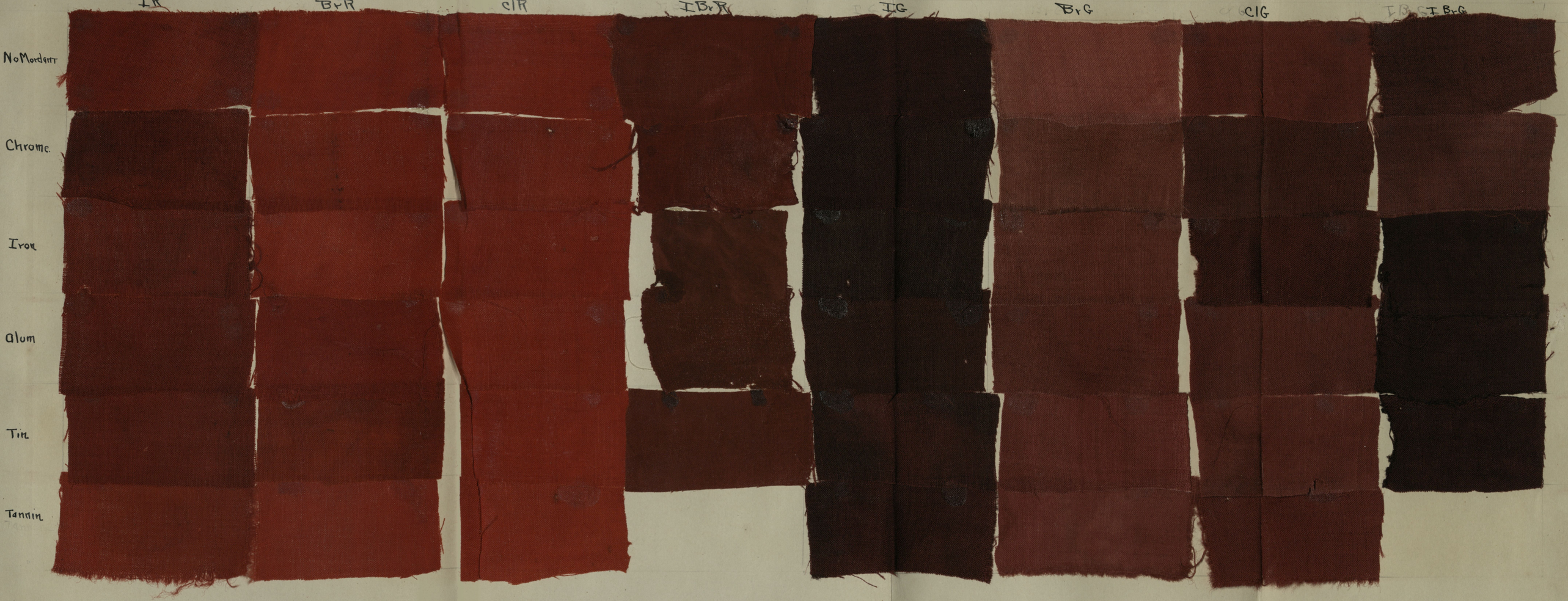
In conclusion I am glad to take this opportunity to express my appreciation to Dr. F. B. Dains for the many helpful suggestions in carrying out this work.

University of Kansas.
May 15, 1917.

Silk


IR
BrR
ClR
IBrR
IG
BrG
ClG
IBrG
No Mordant
Chrome
Iron
Alum
Tin
Tannin

Wool.


IR
BrR
CIR
IBrR
IG
BrG
CIG
IBrG
No Mordant
Chrome
Iron
alum
Tin
Tannin

Cotton.


I R
B R
C I R
I B R
I G
B G
C I G
I B G
No Mordant
Chrome
Iron
alum
Tin
Tannin